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Hydrogen assisted catalytic biomass pyrolysis for green fuels. Effect of catalyst in the fluid bed

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1. Introduction

Fast pyrolysis of biomass is a well-known technology for producing bio-oil. However, in order to use the oil as transportation fuel the oxygen content must be decreased from approximately 40 wt.% to below 1 wt.% [1]. This can be achieved by catalytic hydrodeoxygenation (HDO). Unfortunately, deactivation due to coking of the catalyst is a severe problem for this technology [1]. The objective of the present work is to produce oxygen free gasoline and diesel from biomass by hydrogen assisted catalytic fast pyrolysis.

2. Experimental

Fast pyrolysis of beech wood (feeding rate: 270 g/h) has been performed in 26 bar hydrogen (flow: 55-90 NL/min) in a fluid bed reactor operated at 450 °C with several different catalysts as bed material followed by an additional vapor phase, fixed bed HDO reactor (operated at 370-400 °C) using a sulfided commercial Ni-Mo/Al₂O₃ catalyst. The time on stream varied between 0.75 and 3.5 h. The tested catalysts in the fluid bed include olivine sand (OS), MgAl₂O₄ (MgAl), CoMo/MgAl₂O₄ (CoMo), zeolite HZSM5 mixed with alumina (ZA), NiMo impregnated on zeolite mixed with alumina (NiMoZA), and a cheap and non-toxic catalyst (HYCP). The HYCP catalyst was tested both in reduced (HYCP-R) and sulfided forms (HYCP-S), while the other catalysts, with the exception of OS, were sulfided prior to the experiment.

3. Results and discussion

The product distribution for the experiments where the HDO reactor was used is shown in Figure 1. The obtained bio-oil from these experiments was essentially oxygen free and was in the diesel and gasoline boiling point range. Using MgAl and ZA gave a high char yield and a lower yield of condensable organics compared to the supported active catalysts (CoMo and NiMoZA). Using the HYCP-R catalyst gave a condensable organic yield of 25 wt. % daf corresponding to the highest obtained energy recovery of 58 %. Using the HYCP-R catalyst in the fluid bed reactor and by-passing the HDO reactor decreased the C₁₋₃ yield from 12 to 3 wt. % daf and increased the condensable organic yield from 25 to 34 wt. % daf. However, the oxygen concentration in the produced oil increased to 14 wt. % db. GC×GC-MS/FID showed that the oxygenates were mainly phenols (22 % FID-area) and oxygenated aliphatics (21 % FID area).

The carbon content on the spent catalysts was investigated using scanning electron microscopy (SEM) combined with energy-dispersive X-ray spectroscopy (EDS). This showed that there was up to 3 times as much carbon on the surface of the spent support materials (MgAl and ZA) compared to the supported catalysts (CoMo and NiMoZA) and the HYCP catalysts. Thus, having a more active catalyst in the fluid bed decreases the coking of the catalyst.

4. Conclusions

Our work indicates that hydrogen assisted catalytic pyrolysis is a feasible path for production of liquid renewable fuels. The presence of an active catalyst in the fluid bed is essential and has a significant impact on the product distribution. It is possible to obtain a high yield of condensable organics with the cheap HYCP catalyst, thus showing that it is not necessary to use expensive formulated catalysts. In our ongoing research the differences between CoMo, NiMo and Mo catalysts in the fluid bed is further investigated. Furthermore the effect of the metal loading and the effect of using different supports are also studied and the spent catalysts characterized by use of SEM and transmission electron microscopy (TEM).

References

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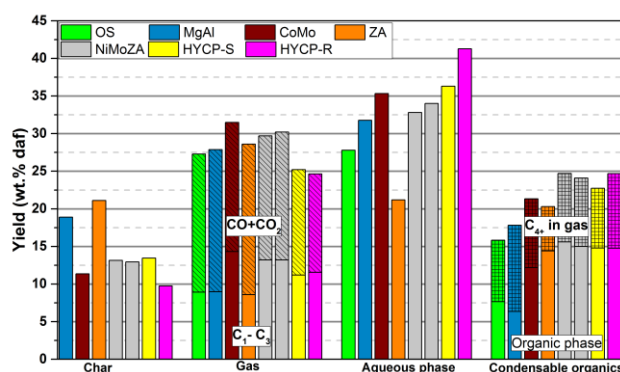


Figure 1. Effect of the catalyst in the fluid bed on the product distribution.